

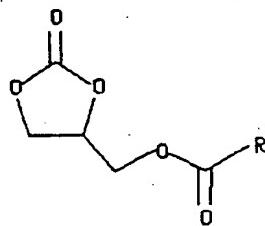
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(54) Title: NOVEL METHODS FOR THE PREPARATION OF GLYCEROL CARBONATE ESTERS



(57) Abstract

Processes for the preparation of glycerol carbonate esters of general formula (I) wherein R is alkyl or alkenyl group having from 1 to about 22 carbon atoms are disclosed. These esters are prepared by reacting glycerol esters of carboxylic acids with a carbonate source in the presence of a catalyst.

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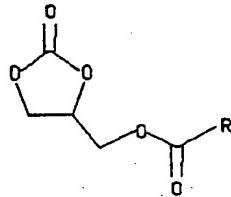
NOVEL METHODS FOR THE PREPARATION
OF GLYCEROL CARBONATE ESTERS
BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates generally to novel methods for the preparation of glycerol carbonate esters having the formula

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wherein R is alkyl or alkenyl group having from 1 to about 22 carbon atoms.

2. Description of the Related Art

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Glycerol carbonate esters are known. See for example U.S. Patent 3,225,063. Glycerol carbonate esters have been prepared by several different methods. A common way to prepare the esters is to allow glycerol carbonate to react with an electrophile such as an acyl chloride. Please see Oehlenschläger, J.; Gerchken, G. Lipids 1978, 13, 557-562.

cyclic anhydrides of dicarboxylic acids have also been reacted with glycerol carbonate to afford the corresponding half ester as described by D'Alelio, G.F. U.S. Patent 3,225,063, 1965. The glycerol carbonate ester of methacrylic acid has been prepared by treating the corresponding glycidyl ester with carbon dioxide as disclosed in Brindöpke, G. U.S. Patent 4,835,289, 1989 and also by a transesterification reaction between glycerol carbonate and methyl methacrylate Fang, J.C.; Hill, S. U.S. patent 2,967,173, 1961. All of the above methods are viable routes to the desired esters, but they are not economically attractive because they require expensive starting materials such as glycerol carbonate or a glycidyl ester or they employ harmful reagents such as carboxylic acid chlorides.

To achieve a desirable synthesis, the ester should be produced economically. Economy in the production of the ester is reflected in both the cost of the starting materials and the length of reaction time and number of steps required to produce the compound.

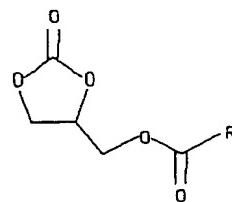
It would therefore be desirable to provide methods of preparing glycerol carbonate ester compounds employing relatively inexpensive starting materials with as few reaction steps as possible, thus lowering the overall cost of the product. Accordingly, it is a primary object of this invention to produce a commercially important glycerol carbonate ester with improved economy.

BRIEF SUMMARY OF THE INVENTION

This invention relates to novel methods for the preparation of glycerol carbonate esters and to their use in reducing the viscosity of surfactants. More particularly, this invention is directed to the preparation of glycerol carbonate esters from starting materials such as feedstocks fats. The compounds of the present invention have the general formula

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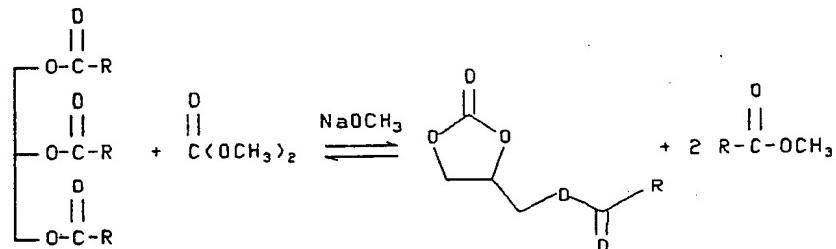
wherein R is alkyl or alkenyl group having from 1 to about 22 carbon atoms.

R as used hereinafter has the same meaning as defined. As examples of alkyl, there may be mentioned methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, eicosyl, and the like. Examples of alkenyl are propenyl, butenyl, hexadecenyl, octadecenyl and the like.

Methods of preparing glycerol carbonate ester compounds in accordance with embodiments of the present invention comprise reacting glycerol esters of carboxylic acids, for example triglyceride compounds with a carbonate source such as di-lower alkyl carbonate or diphenyl carbonate in the presence of a catalyst, for example, strong bases such as alkali metal alkoxides to form the corresponding glycerol carbonate ester of the general formula I and two moles of methyl esters. The reaction may be represented by the scheme below

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wherein R is as defined above. It will be understood by those of ordinary skill in the art that in some instances,

R will be a single alkyl or alkenyl group having from 1 to about 22 carbon atoms. In other cases, R will be a combination of alkyl or alkenyl groups having from 1 to about 22 carbon atoms. For example, one of the R groups could be C₁₃H₂₇, another could be C₁₇H₃₃ while another could be C₁₁H₂₃. In another glycerol ester, two of the R groups could be C₁₇H₃₃ while the other could be C₁₅H₃₁. In cases where the starting glycerol ester is a naturally occurring fat or oil wherein there is usually a distribution of R groups, the glycerol carbonate produced in the process according to the invention will have the same distribution of R groups as the starting glycerol ester. For example, coconut oil is a glycerol triester which typically contains about about 45% lauric acid (R = C₁₁H₂₃), about 18% myristic acid (R = C₁₃H₂₇), and about 11% palmitic acid (R = C₁₅H₃₁). The glycerol carbonate produced in the process according to the invention will contain the same distribution of R groups in the ester product.

In a certain preferred embodiment of the present invention, glycerol esters of carboxylic acids comprise triglycerides and, preferably, naturally occurring triglycerides such as coconut oil, linseed oil, cottonseed oil, palm oil, soybean oil, high-oleic sunflower oil and the like. Preferred triglycerides also comprise glycerol tricaprylate and trilaurate. However, in principle, any natural oil or fat can be used. These naturally occurring oils provide inexpensive routes to preparing the glycerol carbonate ester of general formula I. Preferably, the oil used should have an acid value of up to about 0.1 mg KOH/g. Additionally, di-lower alkyl carbonate may comprise dimethyl carbonate, diethyl carbonate, dipropyl carbonate and the like. Di-lower alkyl carbonate serves as an inexpensive and relatively non-toxic source of carbonate. Diphenyl carbonate may also be advantageously employed. The molar ratio of alkyl carbonate to triglyceride can be from 1/1 to 3/1. The preferred ratio is from 1/1 to 1.5/1

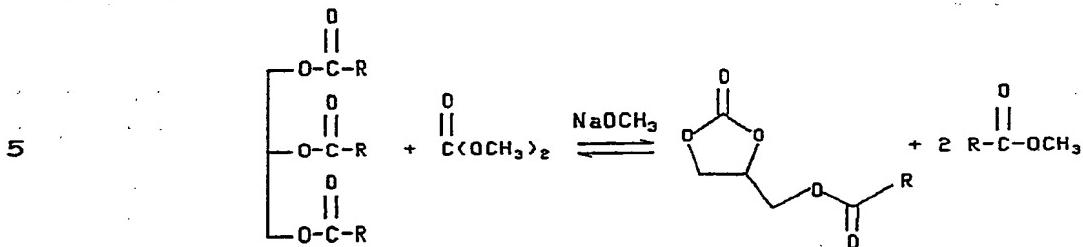
Isolation of the desired glycerol carbonate ester from the crude reaction mixture may be accomplished in a number of ways. For example, a solvent such as diethyl ether, may be added to the crude product mixture followed by aqueous washings, then drying, filtering and concentrating the product. The methyl esters may then be removed by a wiped film evaporation method leaving the glycerol carbonate esters. A preferable method of isolating the glycerol carbonate ester comprises performing aqueous washings of the crude product mixture within the reactor vessel and without using diethyl ether solvent. The crude product can then proceed directly to wiped film evaporation of the methyl esters. It is accordingly a principal object of the present invention to provide novel methods of preparing glycerol carbonate ester compounds.

These and other objects, features and advantages of the present invention may be more clearly understood by considering the following description of specific embodiments.

DESCRIPTION OF SPECIFIC EMBODIMENTS

Examples of R in Formula I are alkyl or alkenyl having from 1 to about 22 carbon atoms. Alkyl may be straight chain, branched or cyclic. As examples of alkyl, there may be mentioned methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, eicosyl, and the like. Preferred examples of alkyl are those corresponding to the naturally occurring triglycerides previously mentioned as starting materials.

The glycerol carbonate esters may be synthesized using a novel one step ester interchange reaction. In a certain preferred embodiment, triglycerides comprising natural oils are reacted with dimethyl carbonate in the presence of a catalyst, e.g. an alkali metal alkoxide, such as sodium methoxide, to produce the desired glycerol carbonate ester along with two moles of methyl ester. This reaction may be represented by the following scheme below



10 wherein R is alkyl or alkenyl group having from 1 to about 22 carbon atoms and preferably R corresponds to alkyl and alkenyl groups in triglycerides comprising natural oils.

Natural oils comprise coconut oil, linseed oil, cottonseed oil, palm oil, soybean oil, high-oleic sunflower 15 oil and the like and preferably, the triglyceride compound has an acid value of up to about 0.1 mg KOH/g. For example, the exchange reaction precedes quite well when food-grade coconut oil (acid value <0.1 mg KOH/g) is used, however when crude coconut oil (acid value = 10.8 mg KOH/g) 20 is used, virtually no reaction is observed. This is thought to be due to the presence of carboxylic acids which react with bases present thus inactivating the catalyst. Also, it is presumed that the carboxylic acid salts will react with any cyclic carbonate formed to afford 25 diglycerides.

The catalyst typically is a strong base comprising 30 preferably alkali metal alkoxides, e.g. sodium methoxide, sodium ethoxide, potassium tert-butoxide, and the like, with sodium methoxide being the preferred catalyst. However, other catalysts such as amidines and cyclic 35 amidines, Na₂CO₃, NaHCO₃, K₂CO₃ and zinc hydroxide of the formula Zn₆Al₂(OH)₁₆(CO₃).4H₂O may also be employed. The reaction may proceed at room temperature, however it is preferably carried out in the temperature range from about 100°C to about 150°C with a more preferable temperature of about 110°C to 140°C. Reaction pressure is the autogenous pressure developed by the reaction mixture in a closed

reactor which may range from about 5 psi to about 100 psi above atmospheric temperature with typical values ranging from about 10 psi to about 50 psi. The reaction may be carried out under an atmosphere of nitrogen, with 5 mechanical stirring until a desired quantity of triglyceride is converted to the desired glycerol carbonate ester. Typical reaction times approach about 4 to about 24 hours, depending upon the nature of the reactants. Longer reaction times lead to greater triglyceride conversion, 10 however, they also lead to decreased yield of glycerol carbonate ester.

The desired product can then be isolated by adding diethyl ether to the crude reaction mixture, followed by aqueous washings, then drying, with $MgSO_4$ filtering and 15 concentrating the product by known techniques such as rotary evaporation. The methyl esters can then be recovered by a wiped film evaporation method. An alternate preferable method of isolating the product comprises performing the aqueous washings within the reactor vessel 20 and without diethyl ether solvent. The crude product can then proceed directly to wiped film evaporation of the methyl esters.

The selected esters of the present invention are useful to lower the viscosity of concentrated aqueous 25 solutions of certain surfactants, such as sulfated ethoxylated fatty alcohols of the general formula $C_{12-14}H_{25-29}O(CH_2CH_2O)_{1-3}OSO_3^-Na^+$. In a commercial embodiment, the composition comprises an effective viscosity reducing amount of the selected esters and the surfactants. The 30 presence of the selected esters reduces the viscosity of concentrated aqueous solutions of the surfactant and permits greater ease of handling.

The following examples set forth certain specific 35 embodiments of the invention and are provided to enable those of skill in the art to practice the invention and, further, to illustrate the utility of the invention in certain applications. These examples should not be

construed to limit the scope of the invention, which is limited only by the lawful scope of the appended claims.

EXAMPLE I

300.6g (0.638 mol) of tricaprylin (Sigma, dried over 5 3A sieves), 86.39g (0.960 mol) of dimethyl carbonate (Aldrich) and 3.89 g (1 wt %) of sodium methoxide (Aldrich) were added to a two liter autoclave. After sealing the autoclave, the contents were mechanically stirred at about 750 rpm and heated to about 130°C with a heating mantle. 10 While at about 130°C, the reaction pressure was approximately 35 psi. After 11 h at about 130°C (tricaprylin conversion > 95%), the reaction mixture was allowed to cool to room temperature. The crude reaction mixture was diluted with 500 ml of ether and subsequently 15 washed with 100 ml of water. The aqueous washing was then extracted with 500 ml of ether. The two ether layers were combined and washed with water (2 x 200 ml) and brine (200 ml). The resulting ether solution was dried over magnesium sulfate, filtered and concentrated by rotary evaporation to 20 give 346.0 g of crude product. The methyl caprylate was then removed by vacuum distillation (head temp.: 27-34°C, vacuum: 122-175 millitorr, pot temp.: 40-50°C) to yield 206.2 g (0.845 mol) of methyl caprylate (99% yield). The residue was then subjected to Kugelrohr distillation 25 (vacuum: 40-50 millitorr, pot temp 110-115°C) to afford 102g of distillate which contained ca. 91 g of the glycerol carbonate ester of caprylic acid (58% yield). The pot residue (15.5g) primarily consisted of tricaprylin about 30 50%, diglycerides about 14% and the glycerol carbonate ester of caprylic acid about 25%.

EXAMPLE II

Experimental-Coconut Oil - 10-Gallon Reactor

To a dry 10 gallon stainless steel reactor the following chemicals were added: 22.5 kg (32.4 mol) of ARGA 35 partially hydrogenated coconut oil, 4.38 kg (48.6 mol, 1.5 equivalents) dimethyl carbonate (DMC), and 0.270 kg (5 moles, 1 wt%) sodium methoxide (NaOMe). The reactor was

then pressure tested to 50 psi with nitrogen. The pressure was reduced to atmospheric pressure and the reactor was sealed.

5 The sealed reactor was heated to 130°C, and mechanically stirred at a rate of 250 rpm. The reaction mixture was heated at 130°C for 24 hours, developing an internal pressure of 17 psi. The reactor was cooled to 50°C and a 2 ml NMR sample was then removed. Proton NMR analysis showed these mol-% values: 22 mol% fatty esters of 10 glycerol carbonate, 60 mol % fatty methyl esters, 4 mol % glycerol carbonate, 3 mol % coconut oil, and 11 mol % DMC.

15 The excess DMC was removed under vacuum (1-2 torr) at 50°C overnight. 0.546 kg of DMC was removed. NMR of the crude product showed that 6.6 mol % DMC remained in the product. Additional DMC was removed from the crude product overnight for ca 16 hours under 1.5 torr vacuum and at a 20 72°C reactor temperature. 0.887 kg DMC was further removed. NMR showed virtually no DMC in the crude product. Total mass of DMC recovered: 1.43 kg (15.9 mol) (0.5 equivalents).

EXAMPLE III

Aqueous Work-Up of the Crude Product

25 The crude product at 50°C was slowly quenched with ca. four liters of ~50°C water, while mechanically stirring at a rate of 100 rpm. The aqueous phase and the organic phase were mixed at a stir rate of 100 rpm for 30 minutes. The mixture was then allowed to separate for 80 minutes. The lower aqueous phase was then removed through a foot valve.

30 The organic phase comprising the crude product was then washed with about four liters of 50°C water at a stir rate of 150 rpm. The aqueous and organic phase were mixed for 30 minutes and then allowed to separate for 40 minutes. Approximately 3 liters of the lower aqueous phase was removed.

35 The organic phase was then washed with about eight liters of 50°C water at a stir rate of 150 rpm. The aqueous and organic phases were mixed for 30 minutes. The

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aqueous and organic phases were allowed to separate for 30 minutes. The lower aqueous phase was then removed through the foot valve.

The organic phase was then washed with about eight liters of 50°C brine at a stir rate of 200 rpm. The aqueous and organic phases were mixed for 30 minutes. The aqueous and organic phases were allowed to separate overnight about 15 hours, and then the aqueous phase was removed through the foot valve. This yielded 23.58 kg of crude product, mass balance: 93%.

EXAMPLE IV

Wiped Film Evaporation (WFE) of the Crude Product

The above product was distilled on a 4 inch wiped-film evaporator. The following conditions were used:

15 First pass: 23.36 kg of crude product was distilled with a jacket temperature of 115°C, a vacuum of 400-500 millitorr and an average feed rate of 0.5 kg/hr. The yield was 11.97 kg residue and 11.16 kg distillate comprising mostly fatty acid methyl esters.

20 Second pass: 11.94 kg of the first pass residue was distilled with a jacket temperature of 125-130°C, a vacuum of 100-135 millitorr and an average feed rate of 0.42 kg/hr. This yielded 8.37 kg of residue and 3.60 kg of distillate.

25 Third pass: 8.37 kg of the second pass residue was
distilled with a jacket temperature of 135°C, a vacuum of
60-110 millitorr and an average feed rate of 0.33 kg/hr.
This yielded 7.00 kg of glycerol carbonate ester residue
and 1.27 kg distillate. The yield of fatty acid ester of
30 glycerol carbonate was 64.3% while the yield of fatty acid
methyl ester was 95.2%.

Pure samples of the glycerol carbonate esters were obtained by further distillation of the third pass residue. The conditions were a jacket temperature of 150°C, a vacuum of 40-100 millitorr and an average feed rate of 0.25 kg/h. The distilled product had purities of 95-97 % as determined by 400 MHz NMR.

EXAMPLE V

Experimental 3 Gallon Reactor

To a dry three-gallon glass reactor the following chemicals were added: 4.94 kg (7.2 mol) of ARGA partially hydrogenated coconut oil. 0.964 kg (10.7 mol, 1.5 equivalents) of DMC, and 0.0590 kg (1.1 mol, 1 wt%) NaOMe.

The above mixture was heated to 130°C for ca 16 hours while mechanically stirring at a rate of 240-260 rpm. A maximum pressure of 15 psi was reached within the glass reactor. The reaction was then cooled to 56°C, and the pressure dropped to 4 psi. A 2 ml NMR sample was removed from the reactor. Mol % analysis by NMR gave the following results: 2 mol% coconut oil, 66 mol% methyl ester, 19 mol% carbonate ester, 11 mol% DMC, and 2 mol% glycerol carbonate. The reaction mixture was heated for an additional 4 hours at 130°C developing an internal pressure of 15 psi. The reactor was cooled and another 2 ml NMR sample was withdrawn. NMR analysis gave the following results: 1 mol% coconut oil, 65 mol% methyl ester, 20 mol% carbonate ester, 10 mol% DMC, 2 mol% glycerol carbonate and 2 mol% unknown carbonate. This NMR showed virtually no change in the composition of the crude product mixture so the reaction was judged complete.

The crude product mixture was then placed under a vacuum of 1-2 torr for three hours. The mass of DMC collected in the traps was 217 g. NMR analysis of the crude product mixture at this point showed 2 mol% DMC remained. The mixture was placed back under vacuum (1-2 torr) at 50°C and left overnight. The following morning NMR analysis of the crude product mixture showed 1.2 mol% DMC still remained. Mass of DMC collected in the traps was 20.1 g. Total DMC removed was 237.1 g.

EXAMPLE VI

Aqueous Work-Up of the Crude Product

The crude product mixture at 50°C was washed with 0.9 L of 50°C water with a stir rate of 50-80 rpm for 15 minutes. The aqueous organic layer was allowed to separate

for 35 minutes. The aqueous layer was then removed through the foot valve. An aqueous/organic emulsion interface containing a dark solid material was also removed.

5 The organic layer was then washed with 1 L of 50°C water at a stir rate of 50-100 rpm for 35 minutes. The mixture was allowed to separate for 15 minutes and then the aqueous layer was removed.

10 The organic layer was then washed with 1.9 L of 50°C water at a stir rate of 60-100 rpm for 35 minutes. The mixture was allowed to separate for 25 minutes and then the aqueous layer was removed.

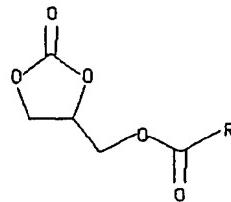
15 The organic layer was then washed with 1.9 L of 50°C brine and stirred for 45 minutes at a rate of 100-170 rpm. The mixture was allowed to separate for 75 minutes and then the aqueous layer was removed.

This yielded 5.31 kg of crude product with a mass balance of 94%.

20 It is to be understood that the embodiment of the invention which has been described is merely illustrative of applications of the principles of the invention. Numerous modifications may be made by those skilled in the art without departing from the true spirit and scope of the invention.

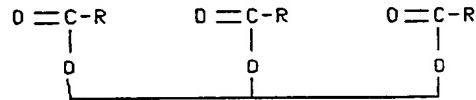
What is claimed is:

1. A process for the preparation of glycerol carbonate esters of the formula



wherein R is alkyl or alkenyl group having from 1 to about 22 carbon atoms comprising treating glycerol esters of carboxylic acids and a carbonate in the presence of a catalyst to form corresponding glycerol carbonate esters.

2. In the process according to claim 1, wherein said glycerol esters of carboxylic acids comprise triglycerides having the general formula



wherein R is alkyl or alkenyl group having from 1 to about 22 carbon atoms.

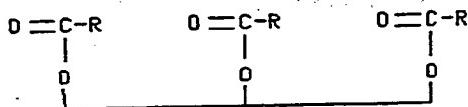
3. In the process according to claim 2, wherein said triglycerides comprise glycerol tricaprylate and glycerol trilauroate.

4. In the process according to claim 2, wherein said triglycerides comprise natural oils.

5. In the process according to claim 4, wherein said natural oils comprise coconut oil, cottonseed oil, linseed oil, palm oil, soybean oil or high oleic sunflower oil.

6. In the process according to claim 4 wherein said natural oils have an acid value of up to about 0.1 mg KOH/g..

7. In the process according to claim 1 wherein said triglycerides comprise natural oils selected from the group consisting of coconut oil, cottonseed oil, linseed oil, palm oil, soybean oil and high oleic sunflower oil, said triglycerides having an acid value of less than about 0.1 and having the general formula



wherein R is alkyl or alkenyl group having from 1 to about 22 carbon atoms.

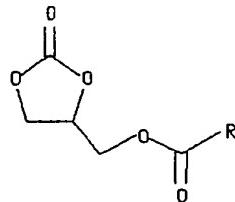
8. In the process according to claim 1 wherein said catalyst comprises alkali metal alkoxides.

9. In the process according to claim 1, wherein said catalyst is a member selected from the group consisting of NaOCH₃, amidines and cyclic amidines, Na₂CO₃, NaHCO₃, K₂CO₃ and zinc hydrotalcite.

10. In the process according to claim 1 wherein said carbonate is di-lower alkyl carbonate or diphenyl carbonate.

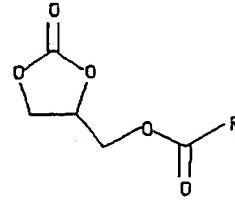
11. In the process according to claim 10 wherein said di-lower alkyl carbonate is dimethyl carbonate, diethyl carbonate or dipropyl carbonate.

12. A process for the preparation of glycerol carbonate esters of the formula



wherein R is alkyl or alkenyl corresponding to alkyl or alkenyl of naturally occurring triglycerides, comprising treating said naturally occurring triglycerides with dimethyl carbonate, diethyl carbonate, dipropyl carbonate or diphenyl carbonate in the presence of alkali metal alkoxides to form corresponding glycerol carbonate esters.

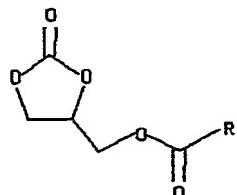
13. A process for the preparation of glycerol carbonate esters of the formula



wherein R is octyl, comprising treating glycerol tricaprylate with dimethyl carbonate in the presence of sodium methoxide to form corresponding glycerol carbonate esters.

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14. A composition comprising a surfactant of the formula $C_{12-14}H_{25-29}O(CH_2CH_2O)_{1-3}OSO_3^-Na^+$ and an amount of glycerol carbonate ester sufficient to lower the viscosity of said surfactant, said glycerol carbonate ester having the formula



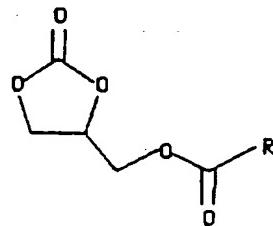
wherein R is alkyl or alkenyl group having from 1 to about 22 carbon atoms in a suitable solvent.



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(54) Title: NOVEL METHODS FOR THE PREPARATION OF GLYCEROL CARBONATE ESTERS



(57) Abstract

Processes for the preparation of glycerol carbonate esters of general formula (I) wherein R is alkyl or alkenyl group having from 1 to about 22 carbon atoms are disclosed. These esters are prepared by reacting glycerol esters of carboxylic acids with a carbonate source in the presence of a catalyst.

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DE	Germany	MG	Madagascar	UA	Ukraine
DK	Denmark	ML	Mali	US	United States of America
ES	Spain	MN	Mongolia	VN	Viet Nam
FI	Finland				

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 91/08049

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)⁶

According to International Patent Classification (IPC) or to both National Classification and IPC
 Int.C1.5 C 07 D 317/36 C 11 D 3/20

II. FIELDS SEARCHED

Minimum Documentation Searched⁷

Classification System	Classification Symbols
Int.C1.5	C 07 D

Documentation Searched other than Minimum Documentation
 to the Extent that such Documents are Included in the Fields Searched⁸

III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹

Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	Lipids, volume 13, no. 8, August 1978, (Champaign, Ill., US) J. Oehlenschlager et al.: "Synthesis and mass spectrometry of 1-acyl and 3-acyl-sn-glycerol carbonates", pages 557-562, see page 558 (cited in the application) -----	1

* Special categories of cited documents : 10

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search

12-06-1992

Date of Mailing of this International Search Report

22 SEP 1993

International Searching Authority

EUROPEAN PATENT OFFICE

Signature of Authorized Officer

R. ENGLISH

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 91/08049

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. **Claims Nos.:**
because they relate to subject matter not required to be searched by this Authority, namely:

2. **Claims Nos.:**
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. **Claims Nos.:**
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. Claims 1-13 Process for the preparation of glycerol carbonate esters
2. Claim 14 Surfactant composition

1. As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1-13

Remark on Protest

- The additional search fees were accompanied by the applicant's protest.
- No protest accompanied the payment of additional search fees.

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- OTHER:** _____

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